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US6136923: Thermoplastic compositions of interpolymers of ethylene with styrene blended with poly vinyl chloride

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Inventor(s): **Cheung; Yunwa W.** , Lake Jackson, TX
Guest; Martin J. , Lake Jackson, TX

Applicant(s): **The Dow Chemical Company**, Midland, MI
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Field of Search: **525/239,214 524/297,130,132,296,298,306,378,527**

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Abstract: The present invention relates to blend compositions comprising; (A) of from about 1 to about 99 weight percent based on the combined weights of Components A, B and C of at least one substantially random interpolpolymer; and wherein said interpolpolymer; (1) contains of from about 0.5 to about 65 mole percent of polymer units derived from; (a) at least one vinylidene aromatic monomer, or (b) at least one hindered aliphatic vinylidene monomer, or (c) a combination of at least one vinylidene aromatic monomer and at least one hindered aliphatic vinylidene monomer; (2) contains of from about 35 to about 99.5 mole percent of polymer units derived from at least one aliphatic .alpha.-olefin having from 2 to 20 carbon atoms; (3) has a molecular weight (Mn) greater than about 1,000; (4) has a melt index (I₂) of from about 0.01 to about 1,000; (5) has a molecular

weight distribution (M_w/M_n) of from about 1.5 to about 20; and (B) of from about 99 to about 1 weight percent based on the combined weights of Components A, B, and C of one or more vinyl halide homopolymer(s) or copolymer(s); and (C) of from about 0 to about 70 weight percent based on the combined weights of Components A, B, and C of one or more plasticizers. The novel blend compositions, provide materials with improved processing/property attributes over the unmodified polymers comprising the blends. The blend compositions can exhibit a unique balance of properties including enhanced modulus and barrier properties, improved tensile strength, radio frequency (rf) sealability, solvent bondability, thermal stability and heat resistance depending upon the selection of the individual blend components and their composition ratios. Additionally, the location and the breadth of the glass transition can be controlled by varying the blend composition and plasticizer level. Surprisingly blends including a plasticizer show a single phase material from glass transition temperature data analysis.

Primary/Assistant
Examiners:
Family:

Wilson; Donald R.;



[Show 66 known family members](#)

U.S. References:

(No patents reference this one)

Patent	Issued	Inventor(s)	Applicant(s)	Title
US4627993	12 /1986	Loomis	E. I. Du Pont de Nemours and Company	Thermoplastic elastomeric compositions based on compatible blends of an ethylene copolymer and vinyl or vinylidene halide polymer
US5244996	9 /1993	Kawaski et al.	Mitsui Petrochemical Industries, Ltd.	Hot-melt adhesive
US5380810	1 /1995	Lai et al.	The Dow Chemical Company	Elastic substantially linear olefin polymers
US5460818	10 /1995	Park et al.	The Dow Chemical Company	Compatibilized blend of olefinic polymers and monovinylidene aromatic polymers
US5576374	11 /1996	Betso et al.	The Dow Chemical Company	Impact modification of filled thermoplastics
US5688866	11 /1997	Silvis et al.	The Dow Chemical Company	Impact modification of thermoplastics
US5739200	4 /1998	Cheung et al.	The Dow Chemical Company	Plasticized .alpha.-olefin/vinylidene aromatic monomer of hindered aliphatic or cycloaliphatic vinylidene monomer interpolymers

First Claim: [Show all 16 claims](#)

What is claimed is:

1. A blend of polymeric materials comprising
 - (A) of from about 1 to about 99 weight percent based on the combined weights of Components A, B and C of at least one substantially random interpolymer; and wherein said interpolymer;
 - (1) contains of from about 0.5 to about 65 mole percent of polymer units derived from styrene;
 - (2) contains of from about 35 to about 99.5 mole percent of polymer units derived from ethylene;
 - (3) has a molecular weight (M_n) greater than about 1,000;
 - (4) has a melt index (I_2 as measured by ASTM D-1238, Condition 190° C./2.16 kg) of from about 0.01 to about 1,000 g/10 min;
 - (5) has a molecular weight distribution (M_w/M_n) of from about 1.5 to about 20; and
 - (B) of from about 99 to about 1 weight percent based on the combined weights of Components A, B, and C of polyvinyl chloride; and
 - (C) of from about 0 to about 70 weight percent based on the combined weights of Components A, B, and C of one or more plasticizers.

Background/Summary:

CROSS-REFERENCE TO RELATED APPLICATIONS

Not Applicable

STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT

Not Applicable

BACKGROUND OF THE INVENTION

This invention relates to thermoplastic compositions of interpolymers of α -olefin monomers with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers blended with vinyl halide homopolymers and copolymers.

The generic class of materials of α -olefin/hindered vinylidene monomer substantially random interpolymers, including materials such as α -olefin/vinyl aromatic monomer interpolymers, and their preparation, are known in the art, such as described in EP 416 815 A2. These materials, such as ethylene/styrene interpolymers, offer a wide range of material structures and properties which makes them useful for varied applications, such as asphalt modifiers or as compatibilizers for blends of polyethylene and polystyrene, as described in U.S. Pat. No. 5,460,818.

The structure, thermal transitions and mechanical properties of substantially random interpolymers of ethylene and styrene containing up to about 50 mole percent styrene have been described (Y. W. Cheung, M. J. Guest; Proc. Antec '96, pages

1634-1637). These polymers are found to have glass transitions in the range -20°C. to $\pm 35^{\circ}\text{C.}$, and show no measurable crystallinity above about 25 mole percent styrene incorporation, i.e. they are essentially amorphous.

Although of utility in their own right, Industry is constantly seeking to improve the applicability of these interpolymers. To perform well in certain applications, these interpolymers could be desirably improved, for example, in the areas of processing characteristics or enhanced glass transition temperature depression or reduced modulus or reduced hardness or lower viscosity or improved ultimate elongation compared to a like property of the unmodified interpolymer. In relation to this invention, it is also considered advantageous to be able to engineer the glass transition process for materials comprising the interpolymers to a particular temperature range, so that the energy absorbing capabilities of the polymer can be best utilized, for example in sound and vibration damping. U.S. Pat. No. 5,739,200 filed Dec. 17, 1996 describes the improvement in properties of interpolymers of α -olefin/vinylidene aromatic monomers obtained by adding plasticizers.

Similarly the family of vinyl polymers such as poly (vinyl chloride) (PVC) have found applications in many markets, in part because of their versatility and good balance. This versatility is readily achieved due to the compatibility of the polymer with a range of plasticizers, typically employed at levels which improve flexibility and processability.

The use of polymeric materials to modify the impact properties of rigid PVC is widely known. For example, the addition of polyacrylic resins, butadiene-containing polymers such as acrylonitrile butadiene styrene terpolymers (ABS), and methacrylate butadiene styrene terpolymers (MBS), and chlorinated polyethylene (CPE) resins to rigid PVC is known to increase the impact strength of PVC products such as house siding panels, vinyl window frames, electrical conduit, and blow molded PVC bottles. Impact modifiers are typically used in these applications at from 5 to about 15 parts by weight per 100 parts of PVC resin. The rigid PVC resins typically used in these applications is typically classified as medium or high molecular weight.

In the case of impact modification of low molecular weight or flexible PVC resins, such as are used in injection molding applications, the melt viscosity of the impact modifying material is higher than that of the PVC resin. This fact can result in poor dispersion and broad particle size distribution of the impact modifier with the effect of the low PVC compounds having low impact strength. Some improvement in impact strength can be gained by increasing the amount of impact modifier in the compound but this is often economically counter-productive.

The purpose of this invention is to provide novel blend compositions comprising one or more vinyl halide polymers and at least one substantially random interpolymer of one or more α -olefin monomers with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers. The novel blend compositions, provide materials with improved processing/property attributes over the unmodified polymers comprising the blends. The blend compositions can exhibit a unique balance of properties including enhanced modulus and barrier properties, improved tensile strength, toughness, radio frequency (rf) sealability, solvent bondability, thermal stability, and ignition resistance, depending upon the selection of the individual blend components and their composition ratios.

As a further embodiment, the invention provides novel blend compositions comprising one or more vinyl halide polymers, and at

least one substantially random interpolpolymer of one or more .alpha.-olefin monomers with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers in combination with one or more plasticizers. These blend compositions allow for the manufacture of materials for which the location and the breadth of the glass transition can be controlled by varying the blend component composition ratio and plasticizer level. Surprisingly certain blends including a plasticizer show a single glass transition temperature (T_g) from thermal analysis data. In other examples, the blend compositions show multiple T_g's, for example when the level of plasticizer is relatively low. Such blend compositions additionally find utility in applications such as sound management and vibration damping.

BRIEF SUMMARY OF THE INVENTION

The present invention relates to blend compositions comprising;

- (A) of from about 1 to about 99 weight percent based on the combined weights of Components A, B and C of at least one substantially random interpolpolymer; and wherein said interpolpolymer;
 - (1) contains of from about 0.5 to about 65 mole percent of polymer units derived from;
 - (a) at least one vinylidene aromatic monomer, or
 - (b) at least one hindered aliphatic vinylidene monomer, or
 - (c) a combination of at least one vinylidene aromatic monomer and at least one hindered aliphatic vinylidene monomer;
 - (2) contains of from about 35 to about 99.5 mole percent of polymer units derived from at least one aliphatic .alpha.-olefin having from 2 to 20 carbon atoms;
 - (3) has a molecular weight (M_n) greater than about 1,000;
 - (4) has a melt index (I₂) of from about 0.01 to about 1,000;
 - (5) has a molecular weight distribution (M_w/M_n) of from about 1.5 to about 20; and
- (B) of from about 99 to about 1 weight percent based on the combined weights of Components A, B, and C of one or more vinyl halide homopolymer(s) or copolymer(s); and
- (C) of from about 0 to about 70 weight percent based on the combined weights of Components A, B, and C of one or more plasticizers.

The compositions of the present invention, can be utilized to produce a wide range of fabricated articles such as, for example, calendered, cast and blown sheets and films and injection molded parts, and the like. The compositions of the present invention can further find utility in flexible molded goods, as layers in multilayer film structures, in applications such as automotive instrument panel skins, as construction materials such as sidings, in flooring systems, as coatings on substrates including polymers, paper, leather, cloth and inorganic building materials, as foams for heat, sound and

vibration damping.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

All references herein to elements or metals belonging to a certain Group refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1989. Also any reference to the Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The term "hydrocarbyl" as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic, aryl substituted cycloaliphatic, aliphatic substituted aromatic, or aliphatic substituted cycloaliphatic groups.

The term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached.

The term "copolymer" as employed herein means a polymer wherein at least two different monomers are polymerized to form the copolymer.

The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer. This includes copolymers, terpolymers, etc.

The term "substantially random" in the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer or hindered aliphatic or cycloaliphatic vinylidene monomer as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Preferably, the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer does not contain more than 15 percent of the total amount of vinylidene aromatic monomer in blocks of vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer was not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-¹³ NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

The Ethylene/Hindered Vinylidene Interpolymers

The substantially random α -olefin/vinylidene aromatic interpolymers blend components of the present invention include, but are not limited to interpolymers prepared by polymerizing one or more α -olefins with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers.

Suitable α -olefins include for example, α -olefins containing from 2 to about 20, preferably from 2 to about 12, more preferably from 2 to about 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 and octene-1. These α -olefins do not contain an aromatic moiety.

Suitable vinylidene aromatic monomers which can be employed to prepare the interpolymers include, for example, those represented by the following formula: [Figure] wherein R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C_{1-4} -alkyl, and C_{1-4} -haloalkyl; and n has a value from zero to about 4, preferably from zero to 2, most preferably zero. Exemplary monovinylidene aromatic monomers include styrene, vinyl toluene, α -methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and the like. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, α -methylstyrene, the lower alkyl- (C_1 - C_4) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof, and the like. A more preferred aromatic monovinylidene monomer is styrene.

By the term "hindered aliphatic or cycloaliphatic vinylidene compounds", it is meant addition polymerizable vinylidene monomers corresponding to the formula: [Figure] wherein A^1 is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; or alternatively R^1 and A^1 together form a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic or cycloaliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl, and the like. Most preferred hindered aliphatic or cycloaliphatic vinylidene compounds are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3- and 4-vinylcyclohexene.

The substantially random interpolymers may be modified by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

One method of preparation of the substantially random interpolymers is by polymerization of a mixture of polymerizable monomers in the presence of metallocene or constrained geometry catalysts and an activating cocatalyst.

The substantially random interpolymers can be prepared as described in U.S. application Ser. No. 545,403 filed Jul. 3, 1990 (corresponding to EP-A-0,416,815) by James C. Stevens et al., both of which are incorporated herein by reference in their entirety. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from -30° C. to 200° C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products for example the production of atactic polystyrene.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. application Ser. No. 545,403, filed Jul. 3, 1990 (EP-A-416,815); U.S. application Ser. No. 702,475, filed May 20, 1991 now abandoned (EP-A-514,828); U.S. Pat. No. 5,721,185, filed May 5, 1992, (EP-A-520,732); U.S. Pat. No. 5,470,993, filed May 12, 1994; as well as U.S. Pat. Nos.: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; and 5,399,635 all of which patents and applications are incorporated herein by reference.

The substantially random .alpha.-olefin/vinylidene aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula [Figure] where Cp¹ and Cp² are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other; R¹ and R² are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxy groups, or aryloxy groups, independently of each other; M is a group IV metal, preferably Zr or Hf, most preferably Zr; and R³ is an alkylene group or silanediyl group used to cross-link Cp¹ and Cp².

The substantially random .alpha.-olefin/vinylidene aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in *Plastics Technology*, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety.

Also suitable are the substantially random interpolymers which comprise at least one .alpha.-olefin/vinyl aromatic/vinyl aromatic/.alpha.-olefin tetrad disclosed in U.S. application Ser. No. 08/708,869 filed Sep. 4, 1996 now abandoned by Francis J. Timmers et al. These interpolymers contain additional signals with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.70-44.25 ppm and 38.0-38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9 and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70-44.25 ppm are methine carbons and the signals in the region 38.0-38.5 ppm are methylene carbons.

It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer insertions preceded and followed by at least one .alpha.-olefin insertion, e.g.

an ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an α -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon-¹³ NMR peaks but with slightly different chemical shifts.

These interpolymers are prepared by conducting the polymerization at temperatures of from about -30° C. to about 250° C. in the presence of such catalysts as those represented by the formula [Figure] wherein: each Cp is independently, each occurrence, a substituted cyclopentadienyl group π -bound to M; E is C or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms; each R' is independently, each occurrence, H, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms or two R' groups together can be a C₁₋₁₀ hydrocarbyl substituted 1,3-butadiene; m is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula: [Figure] wherein each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

Particularly preferred catalysts include, for example, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl)zirconium dichloride, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl)zirconium 1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl)zirconium di-C₁₋₄ alkyl, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl)zirconium di-C₁₋₄ alkoxide, or any combination thereof and the like.

Further preparative methods for the substantially random α -olefin/vinylidene aromatic interpolymers blend components of the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl₃) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am. Chem. Soc. Div. Polym. Chem.) Volume 35, pages 686,687 [1994]) have reported copolymerization using a MgCl₂/TiCl₄/NdCl₃/Al(iBu)₃ catalyst to give random copolymers of styrene and propylene. Lu et al (Journal of Applied Polymer Science, Volume 53, pages 1453 to 1460 [1994]) have described the copolymerization of ethylene and styrene using a TiCl₄/NdCl₃/MgCl₂/Al(Et)₃ catalyst. The manufacture of α -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in U.S. Pat. No. 5,244,996, issued to Mitsui Petrochemical Industries Ltd. All the

Vinyl halide homopolymers and copolymers are a group of resins which use as a building block the vinyl structure $\text{CH}_2=\text{CXY}$, where X is selected from the group consisting of F, Cl, Br, and I and Y is selected from the group consisting of F, Cl, Br, I and H.

The vinyl halide polymer component of the blends of the present invention include but are not limited to homopolymers and copolymers of vinyl halides with copolymerizable monomers such as .alpha.-olefins including but not limited to ethylene, propylene, vinyl esters of organic acids containing 1 to 18 carbon atoms, e.g. vinyl acetate, vinyl stearate and so forth; vinyl chloride, vinylidene chloride, symmetrical dichloroethylene; acrylonitrile, methacrylonitrile; alkyl acrylate esters in which the alkyl group contains 1 to 8 carbon atoms, e.g. methyl acrylate and butyl acrylate; the corresponding alkyl methacrylate esters; dialkyl esters of dibasic organic acids in which the alkyl groups contain 1-8 carbon atoms, e.g. dibutyl fumarate, diethyl maleate, and so forth.

Preferably the vinyl halide polymers are homopolymers or copolymers of vinyl chloride or vinylidene chloride. Poly (vinyl chloride) polymers (PVC) can be further classified into two main types by their degree of rigidity. These are "rigid" PVC and "flexible" PVC. Flexible PVC is distinguished from rigid PVC primarily by the presence of and amount of plasticizers in the resin. Flexible PVC typically has improved processability, lower tensile strength and higher elongation than rigid PVC.

Of the vinylidene chloride homopolymers and copolymers (PVDC), typically the copolymers with vinyl chloride, acrylates or nitriles are used commercially and are most preferred. The choice of the comonomer significantly affects the properties of the resulting polymer. Perhaps the most notable properties of the various PVDC's are their low permeability to gases and liquids, barrier properties; and chemical resistance.

Also included are the various PVC and PVCD formulations containing minor amounts of other materials present to modify the properties of the PVC or PVCD, including but not limited to polystyrene, styrenic copolymers, polyolefins including homo and copolymers comprising polyethylene, and or polypropylene, and other ethylene/.alpha.-olefin copolymers, polyacrylic resins, butadiene-containing polymers such as acrylonitrile butadiene styrene terpolymers (ABS), and methacrylate butadiene styrene terpolymers (MBS), and chlorinated polyethylene (CPE) resins and the like.

Also included in the family of vinyl halide polymers for use as blend components of the present invention are the chlorinated derivatives of PVC typically prepared by post chlorination of the base resin and known as chlorinated PVC, (CPVC). Although CPVC is based on PVC and shares some of its characteristic properties, CPVC is a unique polymer having a much higher melt temperature range (410-450° C.) and a higher glass transition temperature (239-275° F.) than PVC.

Plasticizers

There is a broad knowledge base on the plasticization of PVC, and it is generally known that many thermoplastics can be plasticized. Reference can be made for example to "Plasticizers" in "Modern Plastics Encyclopedia, Mid October 1988 Issue, Volume 65, No. 11, pages 180-184, McGraw Hill, 1989) regarding aspects of this type of technology. Depending upon the polymer type, typical plasticizer families include phosphoric acid derivatives, phthalic acid derivatives, trimellitate esters, benzoates, adipate esters, epoxy compounds, phosphate esters, glutarates and mineral oils. On the

above methods disclosed for preparing the interpolymer component are incorporated herein by reference.

Also included as interpolymer blend components are C_4 - C_7 , isoolefin/para-alkylstyrene interpolymers which are random copolymers of a C_4 to C_7 isomonoolefin, such as isobutylene and a para-alkylstyrene comonomer, preferably para-methylstyrene containing at least about 80%, more preferably at least about 90% by weight of the para isomer. These interpolymers also include functionalized interpolymers wherein at least some of the alkyl substituent groups present in the styrene monomer units contain halogen or some other functional group incorporated by nucleophilic substitution of benzylic halogen with other groups such as alkoxide, phenoxide, carboxylate, thiolate, thioether, thiocarbamate, dithiocarbamate, thiourea, xanthate, cyanide, malonate, amine, amide, carbazole, phthalamide, maleimide, cyanate and mixtures thereof.

Preferred materials may be characterized as isobutylene interpolymers containing the following monomer units randomly spaced along the polymer chain: These functionalized isomonoolefin interpolymers and their method of preparation are more particularly disclosed in U.S. Pat. No. 5,162,445, the complete disclosure of which is incorporated herein by reference.

Most useful of such functionalized materials are elastomeric, random interpolymers of isobutylene and para-methylstyrene containing from about 0.5 to about 20 mole % para-methylstyrene wherein up to about 60 mole % of the methyl substituent groups present on the benzyl ring contain a bromine or chlorine atom, preferably a bromine atom. These polymers have a substantially homogeneous compositional distribution such that at least 95% by weight of the polymer has a para-alkylstyrene content within 10% of the average para-alkylstyrene content of the polymer. More preferred polymers are also characterized by a narrow molecular weight distribution (M_w/M_n) of less than about 5, more preferably less than about 2.5, a preferred viscosity average molecular weight in the range of from about 200,000 up to about 2,000,000, and a preferred number average molecular weight in the range of from about 25,000 to about 750,000, as determined by Gel Permeation Chromatography.

The interpolymers may be prepared by slurry polymerization of the monomer mixture using a Lewis Acid catalyst followed by halogenation, preferably bromination, in solution in the presence of halogen and a radical initiator such as heat and/or light and/or a chemical initiator.

Also preferred are brominated interpolymers which generally contain from about 0.1 to about 5 mole % of bromomethylgroups, most of which is monobromomethyl, with less than 0.05 mole % dibromomethyl substituents present in the copolymer. More preferred interpolymers contain from about 0.05 up to about 2.5 wt % of bromine based on the weight of the interpolymer, most preferably from about 0.05 to 0.75 wt % bromine, and are substantially free of ring halogen or halogen in the polymer backbone chain. These interpolymers, their method of preparation, their method of cure and graft or functionalized polymers derived therefrom are more particularly disclosed in the above referenced U.S. Pat. No. 5,162,445. Such interpolymers are commercially available from Exxon Chemical under the tradename Exxpro.TM. Speciality Elastomers.

Vinyl Halide Homopolymers and Copolymers

basis of their molecular weight, plasticizers are further classified as "monomeric" or "polymeric". In comparison with monomeric plasticizers, polymeric plasticizers generally tend to show higher permanence, lower compatibility, and lower plasticization efficiency. Plasticizers are also classed as "primary", and having high compatibility with a particular polymer, or "secondary" if they have lower compatibility. Mixtures of the two types of plasticizers can be employed to achieve cost/performance balances. Suitable modifiers which can be employed herein as the plasticizer component (C) include at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, adipate esters, epoxy compounds, phosphate esters (triaryl, trialkyl, mixed alkyl aryl phosphates), glutarates and oils.

Particularly suitable phthalate esters include, for example, dialkyl C4-C18 phthalate esters such as diethyl, dibutyl phthalate, diisobutyl phthalate, butyl 2-ethylhexyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, diundecyl phthalate, mixed aliphatic esters such as heptyl nonyl phthalate, di(n-hexyl, n-octyl, n-decyl) phthalate (P610), di(n-octyl, n-decyl) phthalate (P810), and aromatic phthalate esters such as diphenyl phthalate ester, or mixed aliphatic-aromatic esters such as benzyl butyl phthalate or any combination thereof and the like.

Additives

Additives such as antioxidants (e.g., hindered phenols such as, for example, Irganox® 1010), phosphites (e.g., Irgafos® 168), U.V. stabilizers, cling additives (e.g., polyisobutylene), antiblock additives, colorants, pigments, fillers, and the like can also be included in the interpolymers employed in the blends of and/or employed in the present invention, to the extent that they do not interfere with the enhanced properties discovered by Applicants.

The additives are employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer or polymer blend from undergoing oxidation at the temperatures and environment employed during storage and ultimate use of the polymers. Such amount of antioxidants is usually in the range of from 0.01 to 10, preferably from 0.05 to 5, more preferably from 0.1 to 2 percent by weight based upon the weight of the polymer or polymer blend. Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render the polymer or polymer blend antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the desired color from the colorant or pigment. Such additives can suitably be employed in the range of from 0.05 to 50, preferably from 0.1 to 35, more preferably from 0.2 to 20 percent by weight based upon the weight of the polymer or polymer blend. However, in the instance of fillers, they could be employed in amounts up to 90 percent by weight based on the weight of the polymer or polymer blend. Additives such as fillers also play a role in the aesthetics of a final article providing a gloss or matte finish.

The Final Blend Compositions

The compositions of the present invention are prepared by any convenient method, including dry blending the individual components and subsequently melt mixing or melt compounding, either directly in the extruder or mill used to make the finished article

(e.g., the automotive part), or by pre-melt mixing in a separate extruder or mill (e.g., a Banbury mixer).

There are many types of molding operations which can be used to form useful fabricated articles or parts from the present compositions, including thermoforming and various injection molding processes (e.g., that described in Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 264-268, "Introduction to Injection Molding" and on pp. 270-271, "Injection Molding Thermoplastics", the disclosures of which are incorporated herein by reference) and blow molding processes (e.g., that described in Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 217-218, "Extrusion-Blow Molding", the disclosure of which is incorporated herein by reference) and profile extrusion. Also included are direct blending and final part formation in a single melt processing operation to fabricate, for example, sheets and films. Some of the fabricated articles include sports articles, containers such as for food or other household articles, footwear, and automotive articles, such as soft facia. The compositions of the present invention, in combination with the final part forming operation, can be selected to control part aesthetics such as a gloss or matte appearance.

The compositions of the present invention can also find utility as so called plastisols or pastes, in which the polymer components are dispersed in a fluid consisting of the plasticizer. Additional components such as viscosity modifiers, diluents or thickeners are often employed to control rheology. Final formulations may also include stabilizers and fillers such as calcium carbonate, clays, kieselguhr, barytes, silica, mica and talc to control properties and aesthetics. These plastisols or pastes find utility in a range of applications including, but not limited to shaped articles such as toys, gaskets, films and sheets, as coatings on polymeric substrates, paper, leather, cloth, and inorganic building materials, and as foams for heat, sound, and vibration damping. Plastisols can be applied by processes such as dip coating, rotational casting, spray systems and hand molding.

Properties of the Individual Blend Components and the Final Blend Compositions

a) The Ethylene/Hindered Vinylidene Interpolymers

The interpolymers of one or more α -olefins and one or more monovinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers employed in the present invention are substantially random polymers. These interpolymers usually contain from about 0.5 to about 65, preferably from about 1 to about 55, more preferably from about 2 to about 50 mole percent of at least one vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer and from about 35 to about 99.5, preferably from about 45 to about 99, more preferably from about 50 to about 98 mole percent of at least one aliphatic α -olefin having from 2 to about 20 carbon atoms.

The number average molecular weight (M_n) of these interpolymers is usually greater than about 1,000, preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 500,000.

The interpolymers applicable to the present invention can have a melt index (I_2) of from about 0.01 to about 1000, preferably of from about 0.1 to about 100, more preferably of from about 0.5 to about 30 g/10 min.

The polydispersity ratio M_w/M_n of the interpolymers applicable to the present invention is from about 1.5 to about 20, preferably of

from about 1.8 to about 10, more preferably of from about 2 to about 5.

While preparing the substantially random interpolmer, an amount of homopolymer may be formed, for example, due to homopolymerization of the vinylidene aromatic monomer at elevated temperatures. The presence of vinylidene aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated. The vinylidene aromatic homopolymer may be separated from the interpolmer, if desired, by extraction techniques such as selective precipitation from solution with a non solvent for either the interpolmer or the vinylidene aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 20 weight percent, preferably less than 15 weight percent based on the total weight of the interpolymers of atactic vinylidene aromatic homopolymer is present. b) The Vinyl Halide Polymer

Blends were prepared using both flexible and rigid PVC. For the blends containing flexible PVC, samples of 55 and 80 Shore A hardness were prepared. The molecular weight of PVC is commonly expressed in terms of the K value or viscosity number which generally spans from 50 to about 80. The molecular weight increases with increasing K value. Typical MWD (M_w/M_n) for PVC are about 2.0 to 2.5. The following table shows the correlation between K value and M_n .

K	M_n
50	~28,000
80	~80,000

c) The Final Blend Compositions

The blends comprise of from about 1 to about 99 wt % of at least one substantially random interpolmer, preferably of from about 5 to about 95 wt %, more preferably of from about 10 to about 90 wt %.

The blends further comprise 1-99 wt % of at least one vinyl chloride polymer, preferably of from about 5 to about 95 wt %, more preferably of from about 10 to about 90 wt %.

The blends further comprise 0-70 wt. % of at least one plasticizer, preferably of from about 5 to about 50 wt %, more preferably of from about 10 to about 40 wt %.

Drawing Descriptions: [Show drawing descriptions](#)

Description of Preferred Embodiments: [Show description of preferred embodiments](#)

Foreign References:

Publication	Country	Date	IPC Class
EP1991000416815	European Patent Office (EPO)	3 /1991	C08F01000
JP1995007278230	Japan	10 /1995	C08F21002
WO1994000000500	World Intellectual Property Organization (WIPO)	1 /1994	C08F01000
WO1995000027755	World Intellectual Property Organization (WIPO)	10 /1995	C08L02508
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WO1998000010015	World Intellectual Property Organization	3 /1998	C08L

(WIPO)		02302
WO1998000027156	World Intellectual Property Organization (WIPO)	6 / 1998
		C08L 02508

Other Abstract Info: CHEMABS 130(22)297435W DERABS C1999-277611

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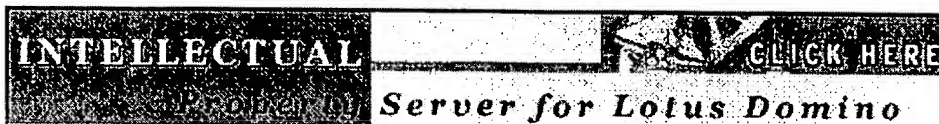


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US5739200: Plasticized .alpha.-olefin/vinylidene aromatic monomer of hindered aliphatic or cycloaliphatic vinylidene monomer interpolymers

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Inventor(s): **Cheung; Yunwa W.** , Lake Jackson, TX
Gathers; John J. , Pearland, TX
Guest; Martin J. , Lake Jackson, TX
Bethea; James R. , Baton Rouge, LA

Applicant(s): **The Dow Chemical Company**, Midland, MI
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Issued/Filed Dates: **April 14, 1998** / Dec. 17, 1996

Application Number: **US1996000767609**

IPC Class: **C08K 5/01;**

ECLA Code: **C08K5/00P1+L25/02;**

Class: **Current:** [524/504](#); [428/412](#); [428/500](#); [524/115](#); [524/296](#); [524/513](#); [524/537](#); [525/107](#); [525/108](#);
Original: [524/504](#); [428/412](#); [428/500](#); [524/115](#); [524/296](#); [524/513](#); [524/537](#); [525/107](#); [525/108](#);

Field of Search: **524/296,297,115,504,513,537 526/347 525/107,108 428/412,500**

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Abstract: Properties of interpolymers of .alpha.-olefin/vinylidene aromatic monomer are enhanced with plasticizers selected from phthalate esters, trimellitate esters, benzoates, aliphatic diesters, epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils. These plasticized interpolymers are useful in a wide range of applications including films, sheet, adhesives, sealants and molded parts.

Primary/Assistant Examiners: **Marquis; Melvyn I.**; Aylward; D.

U.S. References: Show the 2 patents that reference this one

Patent	Issued	Inventor(s)	Applicant(s)	Title
<u>US3228896*</u>	1 /1966	Canterino et al.		
<u>US3740279</u>	6 /1973	Levering et al.		ETHYLENE COPOLYMER COMPOSITE PROPELLANT
<u>US3821149</u>	6 /1974	Makowski et al.	Esso Research and Engineering Company	PLASTICIZED THERMOPLASTIC SEMICRYSTALLINE BLOCK COPOLYMERS
<u>US5414040</u>	5 /1995	McKay et al.	The Dow Chemical Company	Formulated ethylene/ alpha.-olefin elastomeric compounds
<u>US5460818</u>	10 /1995	Park et al.	The Dow Chemical Company	Compatibilized blend of olefinic polymers and monovinylidene aromatic polymers
* some details unavailable				

First Claim: Show all 12 claims

We claim:

1. A composition comprising
 - (A) from about 50 to about 99 percent by weight of at least one substantially random interpolymer comprising
 - (1) from about 5 to about 65 mole percent of polymer units derived from
 - (a) at least one vinylidene aromatic monomer, or
 - (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
 - (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
 - (2) from about 35 to about 95 mole percent of polymer units derived from at least one C₂₋₂₀ .alpha.-olefin; and
 - (B) from about 1 to about 50 percent by weight of at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters, epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils.

Background/Summary:

BACKGROUND OF THE INVENTION

The present invention pertains to the modification of compositions containing interpolymers of .alpha.-olefin/vinylidene aromatic and/or hindered aliphatic and/or cycloaliphatic vinylidene monomer by the use of plasticizer.

The generic class of materials of .alpha.-olefin/hindered vinylidene monomer substantially random interpolymers, including materials such as .alpha.-olefin/vinyl aromatic monomer interpolymers, and their preparation, are known in the art, such as described in EP 416 815 A2. These materials offer a wide range of material structures and properties which makes them useful for varied applications, such as asphalt modifiers or as compatibilizers for blends of polyethylene and polystyrene, as described in U.S. Pat. No. 5,460,818.

The structure, thermal transitions and mechanical properties of substantially random interpolymers of ethylene and styrene containing up to about 50 mole percent styrene have been described (see Y. W. Cheung, M. J. Guest; Proc. Antec '96 pages 1634-1637). These polymers are found to have glass transitions in the range -20° C. to +35° C., and show no measurable crystallinity above about 25 mole percent styrene incorporation, i.e. they are essentially amorphous.

Although of utility in their own right, Industry is constantly seeking to improve the applicability of these interpolymers. To perform well in certain applications, these interpolymers could be desirably improved, for example, in the areas of processing characteristics or enhanced glass transition temperature depression or reduced modulus or reduced hardness or lower viscosity or improved ultimate elongation compared to a like property of the unmodified interpolymer. In relation to this invention, it is also considered advantageous to be able to engineer the glass transition process for the interpolymers to a particular temperature range, so that the energy absorbing capabilities of the polymer can be best utilized for example in sound and vibration damping.

This invention discloses the utility of plasticizers to achieve modification of the .alpha.-olefin/hindered vinylidene monomer substantially random interpolymers. There is a broad knowledge base on the plasticization of poly(vinyl chloride) (PVC), and it is generally known that many thermoplastics can be plasticized. Reference can be made for example to "Plasticizers" in "The Encyclopedia of Polymer Science and Engineering" (Supplement Volume; Wiley Interscience, 1989) regarding this type of technology. Depending upon the polymer type, typical plasticizer families include phosphoric acid derivatives, phthalic acid derivatives, trimellitate esters, benzoates, adipate esters, epoxy compounds, phosphate esters, glutarates and mineral oils. On the basis of their molecular weight, plasticizers are further classified as "monomeric" or "polymeric". In comparison with monomeric plasticizers, polymeric plasticizers generally tend to show higher permanence, lower compatibility, and lower plasticization efficiency. Plasticizers are also classed as "primary", and having high comparability with a particular polymer, or "secondary" if they have lower compatibility. Mixtures of the various types of plasticizers can be employed to achieve cost/performance balances.

One well known effect of the addition of small amounts of plasticizer is that many polymers, including polystyrene, polycarbonate, and Nylon 66 exhibit "anti-plasticization" in which significant increases in modulus and tensile strength and loss of toughness are observed. This effect is also found for PVC when plasticizers are utilized at relatively low concentrations of up to about 10-17 weight percent, depending on the plasticizer nature. Because

of antiplasticization effects, compositions including less than about 20 parts per hundred of PVC are seldom encountered.

Based on the available background information, combinations of .alpha.-olefin/hindered vinylidene monomer substantially random interpolymers, and especially ethylene/styrene interpolymers, with typical plasticizers associated with PVC modification would not appear to offer an effective route to modify their performance. It is well-known that amorphous thermoplastic polymers, such as atactic polystyrene, will accept large amounts of plasticizers, and although they lower the glass transition temperature they rapidly form gums or liquids, i.e. they have no function as solid-state polymers. Addition of small (less than 3 weight percent) of dibutyl phthalate (DBP) has been used in latex formulations used for polish based on thermoplastics including polystyrene. The compatibility of vinyl-type plasticizers with low density polyethylene (LDPE) is usually about 0 to 2 weight percent, although some hydrocarbons such as certain mineral oils may be compatible up to about 20 weight percent. U.S. Pat. No. 3,821,149 describing "Plasticized thermoplastic semi-crystalline block copolymers" teaches that random copolymers of ethylene and t-butyl styrene are non-crystalline, and when plasticized with 50 to 100 parts of dibutyl phthalate provides a product of little desirable physical properties. Random and statistical copolymers are specifically excluded from U.S. Pat. No. 3,821,149.

A further approach to consider regarding plasticization is the relative compatibility of the plasticizing molecule with the polymer. Reference to Buszard ("Theoretical Aspects of Plasticization" in "PVC Technology; Fourth Edition" ed. W. V. Titow, Applied Science Publishers 1984) outlines theoretical techniques for assessing the compatibility, and hence utility of plasticizers with PVC by the use of the solubility parameter. The matching of solubility parameters of polymer and effective plasticizers is one guide to defining nominal compatibility. Although there are some assumptions and limitations in adopting this approach, in general it is evident that effective plasticizers will have good compatibility or miscibility with the polymer. Reference to "Polymer Handbook" (Third edition, ed. J. Brandrup, E. H. Immergut, Wiley Interscience, 1989) gives the solubility parameter of PVC as around $19.8(\text{MPa})^{0.5}$, and appropriate plasticizers have solubility parameters which fall between the limits of $17.2(\text{MPa})^{0.5}$ and $23.3(\text{MPa})^{0.5}$.

The reported solubility parameters of poly(ethylene) and poly(styrene) are $16.2(\text{MPa})^{0.5}$ and $18.6(\text{MPa})^{0.5}$ respectively. Based on group additivity theories, it is expected that substantially random copolymers of ethylene and styrene will have solubility parameters falling somewhere between these values.

It is not anticipated that interpolymers which are rich in ethylene would be effectively modified by many typical plasticizers used for vinyl modification, because of the differences in solubility parameters between polymer and plasticizer. Additionally, it is not anticipated that interpolymers which are relatively rich in styrene (~25-60 mole percent), and amorphous in nature, would be effectively modified by many typical plasticizers used for vinyl modification.

Based on the available background information, it would not be anticipated that .alpha.-olefin/hindered vinylidene monomer substantially random interpolymers, and especially ethylene/styrene interpolymers, would be effectively modified by many typical plasticizers associated with PVC modification, and particularly in the ranges of plasticizer incorporation described in this invention.

SUMMARY OF THE INVENTION

One aspect of the present invention pertains to a composition comprising

- (A) from about 50 to about 99 percent by weight of at least one substantially random interpolymer resulting from polymerizing a monomer composition comprising
- (1) from about 1 to about 65 mole percent of
 - (a) at least one vinylidene aromatic monomer, or
 - (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
 - (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
- (2) from about 35 to about 99 mole percent of at least one C₂-₂₀ .alpha.-olefin; and
- B) from about 1 to about 50 percent by weight of at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters (including adipates azelates and sebacates), epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils.

Another aspect of the present invention pertains to such modified interpolymers in the form of a film or sheet, or as a component of a multilayered structure resulting from calendering, blowing, casting or (co)extrusion operations.

Another aspect of the present invention pertains to such modified interpolymers and their utility in the form of foams, fibers or emulsions.

Another aspect of the present invention pertains to the utilization of such modified interpolymers in adhesives, adhesive formulations and adhesive/sealant applications.

Another aspect of the present invention pertains to injection, compression, extruded or blow molded parts prepared from such modified interpolymers.

The compositions of the present invention can "comprise", "consist essentially of" or "consist of" any two or more of such polymers or interpolymers or plasticizers enumerated herein.

These compositions provide an improvement in one or more of the properties such as, but not limited to, processing characteristics or enhanced glass transition temperature depression or reduced modulus or reduced hardness or lower viscosity or improved ultimate elongation compared to a like property of the unmodified interpolymer.

Drawing Descriptions: [Show drawing descriptions](#)

Description of Preferred Embodiments: [Show description of preferred embodiments](#)

Embodiments:

Foreign References: **none**

(No patents reference this one)

Other Abstract Info: CHEMABS 128(21)258064P CAN128(21)258064P

Other References:

- Derwent Abstract 91-166077/23 (EP 430,538-A).

Article info links by



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- Derwent Abstract 95-280994/37 (JP 07-179,614-A).
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- Derwent Abstract 93-285115/36 (JP 05-200,892-A).



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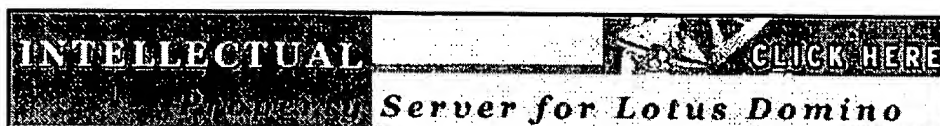
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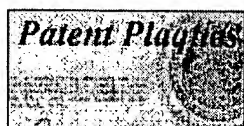
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US5739200: Plasticized .alpha.-olefin/vinylidene aromatic monomer of hindered aliphatic or cycloaliphatic vinylidene monomer interpolymers

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Inventor(s): **Cheung; Yunwa W.** , Lake Jackson, TX
Gathers; John J. , Pearland, TX
Guest; Martin J. , Lake Jackson, TX
Bethea; James R. , Baton Rouge, LA

Applicant(s): **The Dow Chemical Company**, Midland, MI
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Issued/Filed Dates: **April 14, 1998** / Dec. 17, 1996

Application Number: **US1996000767609**

IPC Class: **C08K 5/01;**

ECLA Code: **C08K5/00P1+L25/02;**

Class: **Current:** [524/504](#); [428/412](#); [428/500](#); [524/115](#); [524/296](#); [524/513](#); [524/537](#); [525/107](#); [525/108](#);
Original: [524/504](#); [428/412](#); [428/500](#); [524/115](#); [524/296](#); [524/513](#); [524/537](#); [525/107](#); [525/108](#);

Field of Search: **524/296,297,115,504,513,537** [526/347](#) [525/107,108](#) [428/412,500](#)

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Abstract: Properties of interpolymers of .alpha.-olefin/vinylidene aromatic monomer are enhanced with plasticizers selected from phthalate esters, trimellitate esters, benzoates, aliphatic diesters, epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils. These plasticized interpolymers are useful in a wide range of applications including films, sheet, adhesives, sealants and molded parts.

Primary/Assistant Examiners: **Marquis; Melvyn I.**; Aylward; D.

U.S. References: [Show the 2 patents that reference this one](#)

Patent	Issued	Inventor(s)	Applicant(s)	Title
US3228896*	1 /1966	Canterino et al.		
US3740279	6 /1973	Levering et al.		ETHYLENE COPOLYMER COMPOSITE PROPELLANT
US3821149	6 /1974	Makowski et al.	Esso Research and Engineering Company	PLASTICIZED THERMOPLASTIC SEMICRYSTALLINE BLOCK COPOLYMERS
US5414040	5 /1995	McKay et al.	The Dow Chemical Company	Formulated ethylene/alpha.-olefin elastomeric compounds
US5460818	10 /1995	Park et al.	The Dow Chemical Company	Compatibilized blend of olefinic polymers and monovinylidene aromatic polymers
* some details unavailable				

First Claim: [Show all 12 claims](#)

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 - (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
 - (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
 - (2) from about 35 to about 95 mole percent of polymer units derived from at least one C₂₋₂₀ alpha.-olefin; and
 - (B) from about 1 to about 50 percent by weight of at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters, epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils.

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Description of

DETAILED DESCRIPTION OF THE INVENTION

Preferred
Embodiments:

The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer.

The term "copolymer" as employed herein means a polymer wherein at least two different monomers are polymerized to form the copolymer.

The term "substantially random" in the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer or hindered aliphatic or cycloaliphatic vinylidene monomer as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Preferably, the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer does not contain more than 15 percent of the total amount of vinylidene aromatic monomer in blocks of vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer was not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-¹³ NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The interpolymers suitable for blending to make the blends comprising the present invention include, but are not limited to interpolymers prepared by polymerizing one or more α -olefins with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers.

Suitable α -olefins include for example, α -olefins containing from 2 to about 20, preferably from 2 to about 12, more preferably from 2 to about 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 and octene-1. These α -olefins do not contain an aromatic moiety.

Suitable vinylidene aromatic monomers which can be employed to prepare the interpolymers employed in the blends include, for example, those represented by the following formula: [Figure] wherein R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R² is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group

substituted with from 1 to 5 substituents selected from the group consisting of halo, C₁₋₄-alkyl, and C₁₋₄-haloalkyl; and n has a value from zero to about 4, preferably from zero to 2, most preferably zero. Exemplary monovinylidene aromatic monomers include styrene, vinyl toluene, .alpha.-methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and the like. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, .alpha.-methyl styrene, the lower alkyl- (C₁-C₄) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof, and the like. A more preferred aromatic monovinylidene monomer is styrene.

By the term "hindered aliphatic or cycloaliphatic vinylidene compounds", it is meant addition polymerizable vinylidene monomers corresponding to the formula: [Figure] wherein A¹ is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R² is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; or alternatively R¹ and A¹ together form a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic or cycloaliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl, and the like. Most preferred hindered aliphatic or cycloaliphatic vinylidene compounds are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene.

The interpolymers of one or more .alpha.-olefins and one or more monovinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers employed in the present invention are substantially random polymers. These interpolymers usually contain from about 5 to about 65, preferably from about 5 to about 50, more preferably from about 10 to about 50 mole percent of at least one vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer and from about 35 to about 95, preferably from about 50 to about 95, more preferably from about 50 to about 90 mole percent of at least one aliphatic .alpha.-olefin having from 2 to about 20 carbon atoms.

The number average molecular weight (Mn) of the polymers and interpolymers is usually greater than about 10,000, preferably from about 20,000 to about 1,000,000, more preferably from about 50,000 to about 500,000.

While preparing the substantially random interpolymers, an amount of atactic vinylidene aromatic homopolymer may be formed due to homopolymerization of the vinylidene aromatic monomer at elevated temperatures. The presence of vinylidene aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated. The vinylidene aromatic homopolymer may be separated from the interpolymers, if desired, by extraction techniques.

such as selective precipitation from solution with a non solvent for either the interpolymers or the vinylidene aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 20 weight percent, preferably less than 15 weight percent based on the total weight of the interpolymers of vinylidene aromatic homopolymer is present.

The substantially random interpolymers may be modified by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

The substantially random interpolymers can be prepared as described in U.S. application Ser. No. 07/545,403 filed Jul. 3, 1990 pending (corresponding to EP-A-0,416,815) by James C. Stevens et al. and is allowed U.S. application Ser. No. 08/469,828 filed Jun. 6, 1995 all of which are incorporated herein by reference in their entirety. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3,000 atmospheres and temperatures from -30° C. to 200° C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. application Ser. No. 07/545,403, filed Jul. 3, 1990 pending corresponding to EP-A-416,815; U.S. application Ser. No. 07/702,475, filed May 20, 1991 abandoned corresponding to EP-A-514,828; U.S. application Ser. No. 07/876,268, filed May 1, 1992 allowed corresponding to EP-A-520,732; U.S. application Ser. No. 08/241,523, filed May 12, 1994 U.S. Pat. No. 5,470,993; as well as U.S. Pat. Nos.: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635 and 5,556,928 all of which patents and applications are incorporated herein by reference in their entirety.

The substantially random .alpha.-olefin/vinylidene aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety.

Also suitable are the substantially random interpolymers which comprise at least one .alpha.-olefin/vinyl aromatic/vinyl aromatic/.alpha.-olefin tetrad disclosed in U.S. application Ser. No. 08/708,869 filed Sep. 4, 1996 pending by Francis J. Timmers et al. These interpolymers contain additional signals with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.75-44.25 ppm and 38.0-38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9 and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.75-44.25 ppm are methine carbons and the signals in the region 38.0-38.5 ppm are methylene carbons.

In order to determine the carbon-¹³ NMR chemical shifts of the interpolymers described, the following procedures and conditions are employed. A five to ten weight percent polymer solution is prepared in a mixture consisting of 50 volume percent 1,1,2,2-tetrachloroethane-d₂ and 50 volume percent 0.10 molar chromium tris(acetylacetonate) in 1,2,4-trichlorobenzene. NMR spectra are acquired at 130° C. using an inverse gated decoupling sequence, a 90° pulse width and a pulse delay of five seconds or more. The spectra are referenced to the isolated methylene signal of the

polymer assigned at 30.000 ppm.

It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer preceded and followed by at least one α -olefin insertion, e.g. an ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an α -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon-¹³ NMR peaks but with slightly different chemical shifts.

These interpolymers are prepared by conducting the polymerization at temperatures of from about -30° C. to about 250° C. in the presence of such catalysts as those represented by the formula [Figure] wherein: each Cp is independently, each occurrence, a substituted cyclopentadienyl group π -bound to M; E is C or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms; each R' is independently, each occurrence, H, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms or two R' groups together can be a C₁₋₁₀ hydrocarbyl substituted 1,3-butadiene; m is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. Particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula: [Figure] wherein each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

Particularly preferred catalysts include, for example, racemic (dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium dichloride, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium 1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium di-C₁₋₄ alkyl, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl)) zirconium di-C₁₋₄ alkoxide, or any combination thereof and the like.

Further preparative methods for the interpolymer component (A) of the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl₃) to prepare an ethylenestyrene copolymer. Xu and Lin (Polymer Preprints, Am.Chem.Soc., Div.Polym.Chem.) Volume 35, pages 686,687 [1994]) have reported copolymerization using a MgCl₂/TiCl₄/NdCl₃/Al(iBu)₃ catalyst to give random copolymers of styrene and propylene. Lu et al (Journal of Applied Polymer Science, Volume 53, pages 1453 to 1460 [1994]) have described the copolymerization of

ethylene and styrene using a TiCl_4 / NdCl_3 / MgCl_2 / $\text{Al}(\text{Et})_3$ catalyst.

The manufacture of .alpha.-olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in U.S. Pat. No. 5,244,996, issued to Mitsui Petrochemical Industries Ltd. All the above methods disclosed for preparing the interpolymers are incorporated herein by reference.

Suitable modifiers which can be employed herein as the plasticizer component (B) include at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters (including adipates azelates and sebacates), epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils.

Particularly suitable phthalate esters include, for example, dialkyl C_4 - C_{18} phthalate esters such as diethyl, dibutyl phthalate, diisobutyl phthalate, butyl 2-ethylhexyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, diundecyl phthalate, mixed aliphatic esters such as heptyl nonyl phthalate, di(n-hexyl, n-octyl, n-decyl) phthalate (P610), di(n-octyl, n-decyl) phthalate (P810), and aromatic phthalate esters such as diphenyl phthalate ester, or mixed aliphatic-aromatic esters such as benzyl butyl phthalate or any combination thereof and the like.

Particularly suitable trimellitate esters include, for example, tri(2-ethylhexyl) trimellitate, tri(heptyl, nonyl) trimellitate, tri isooctyl trimellitate, tri isodecyl trimellitate, tri (octyl, decyl) trimellitate.

Particularly suitable benzoates include, for example, diethylene glycol dibenzoate and dipropylene glycol dibenzoate.

Particularly suitable epoxy compounds include, for example, epoxidised vegetable oils such as epoxidised soyabean oil and epoxidised linseed oil.

Particularly suitable phosphate esters include, for example, triaryl, trialkyl, mixed alkyl aryl phosphates such as tributyl phosphate, trioctyl phosphate, tri(2-ethylhexyl) phosphate, tributoxyethyl phosphate, triphenyl phosphate, tricresyl phosphate, isopropylphenyl diphenyl phosphate, t-butylphenyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate and isodecyl diphenyl phosphate.

Particularly suitable oils include, for example, mineral oils, natural oils, naphthenic oils, paraffinic oils and aromatic oils.

The compositions of the present invention suitably comprise from about 50 to about 99, preferably from about 55 to about 95, more preferably from about 60 to about 90, percent by weight based on the combined weight of components (A) and (B) of the interpolymers (s) of .alpha.-olefin/vinylidene aromatic monomer and/or hindered aliphatic and/or cycloaliphatic vinylidene monomer as component (A); and from about 1 to about 50, preferably from about 5 to about 45, more preferably from about 10 to about 40, percent by weight based on the combined weight of components (A) and (B) of plasticizer(s) as component (B).

The compositions of the present invention may be prepared by any suitable means known in the art such as, but not limited to, dry blending in a pelletized form in the desired proportions followed by melt blending in a screw extruder, an internal batch mixer e.g. a Banbury mixer, a calender or a roll mill, or the like.

Additives such as antioxidants (e.g., hindered phenols such as, for example, IRGANOX.TM. 1010), phosphites (e.g., IRGAFOS® 168)), U. V. stabilizers, cling additives (e.g., PIB), antiblock additives, slip agents, colorants, pigments, fillers, and the like can also be included in the interpolymers employed in the blends of the present invention, to the extent that they do not interfere with the enhanced properties discovered by Applicants. Minor amounts, up

to 50 percent by weight, of other polymers including polystyrene, syndiotactic polystyrene, styrenic copolymers such as styrene/acrylonitrile, polyolefin homo and copolymers, polyethylene, polypropylene, poly(vinyl chloride), polycarbonate, polyethylene terephthalate, urethane polymers and polyphenylene oxide, can also be included in the interpolymers employed in the blends of the present invention, to the extent that they do not interfere with the enhanced properties discovered by Applicants.

The additives are employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer or polymer blend from undergoing oxidation at the temperatures and environment employed during storage and ultimate use of the polymers. Such amounts of antioxidants is usually in the range of from about 0.01 to about 10, preferably from about 0.05 to about 5, more preferably from about 0.1 to about 2 percent by weight based upon the weight of the polymer or polymer blend.

Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render the polymer or polymer blend antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the desired color from the colorant or pigment. Such additives can suitably be employed in the range of from about 0.05 to about 50, preferably from about 0.1 to about 35 more preferably from about 0.2 to about 20 percent by weight based upon the weight of the polymer or polymer blend. However, in the instance of fillers, they could be employed in amounts up to about 90 percent by weight based on the weight of the polymer or polymer blend.

The compositions of the present invention can be utilized to produce, but not limited to, a wide range of fabricated articles such as, for example, calendered sheet, blown films and injection molded parts, and the like. The compositions can also be used in the manufacture of fibers, foams and latices. The compositions of the present invention can also be utilized in adhesive and sealant formulations.

The following examples are illustrative of the invention, but are not to be construed as to limiting the scope of the invention in any manner.

Preparation of Interpolymers (A), (B), (C), and (D)

Polymer is prepared in a 400 gallon agitated semi-continuous batch reactor. The reaction mixture consisted of approximately 250 gallons a solvent comprising a mixture of cyclohexane (85 wt %) & isopentane (15 wt %), and styrene. Prior to addition, solvent, styrene and ethylene are purified to remove water and oxygen. The inhibitor in the styrene is also removed. Inerts are removed by purging the vessel with ethylene. The vessel is then pressure controlled to a set point with ethylene. Hydrogen is added to control molecular weight. Temperature in the vessel is controlled to set-point by varying the jacket water temperature on the vessel. Prior to polymerization, the vessel is heated to the desired run temperature and the catalyst components: Titanium: (N-1,1-dimethylethyl)-dimethyl(1-(1,2,3,4,5-eta)-2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silanaminato))(2-) N)-dimethyl, CAS# 135072-62-7, Tris(pentafluorophenyl)boron, CAS# 001109-15-5, Modified methylaluminoxane Type 3A, CAS# 146905-79-5, are flow controlled, on a mole ratio basis of 1/3/5 respectively, combined and added to the vessel. After starting, the polymerization is allowed to proceed with ethylene supplied to the reactor as required to maintain vessel pressure. In some cases, hydrogen is added to the headspace of the reactor to maintain a

mole ratio with respect to the ethylene concentration. At the end of the run, the catalyst flow is stopped, ethylene is removed from the reactor, about 1000 ppm of Irganox.TM. 1010 anti-oxidant is then added to the solution and the polymer is isolated from the solution. The resulting polymers are isolated from solution by either stripping with steam in a vessel or by use of a devolatilizing extruder. In the case of the steam stripped material, additional processing is required in extruder like equipment to reduce residual moisture and any unreacted styrene. Table 1 provides a summary of the process conditions used to produce the polymers, together with characterization data.

TABLE 1

Total Polym.	
Solvent	
Styrene H ₂	
Run	
in	
Sample	
loaded loaded Pressure	
Temp.	
Added	
Time	
Solution	
Number	
lbs kg lbs kg Psig	
kPa	
°C.	
Gms Hrs	
Wt. %	
A 252 114	
1320	
599	
42 290	
60 0 2.8	
11.5	
B 252 114	
1320	
599	
40 276	
60 23 6.5	
18.0	
C 842 382	
662 300	
105	
724	
60 8.8 3.7	
8.6	
D 1196	
542	
225 102	
70 483	
60 7.5 6.1	
7.2	
Total Wt % Styrene	
Talc Level	
Isolation	
Sample Number	
Melt Index	
in Polymer*	
Wt % Method	
A 0.18 81.7 <2.5 Stm. Str.	
B 1.83 81.6 <2.0 Stm. Str.	
C 0.01 48.3 <1.0 Stm. Str.	
D 0.03 29.8 0 Extruder	
*Styrene content measured by FTIR technique	

Test parts and characterization data for the interpolymers and the blends are generated according to the following procedures:

Part Preparation and Testing Procedures

The plasticizers employed were: P610, a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester having a molecular weight(MW) of about 400 available from the C. P. Hall Co.; G57 is a "polymeric" (MW~5,700) glutarate available from the C. P. Hall Co. and Sunpar 2280, a paraffinic oil available from Sun Company, Inc. and having a molecular weight of 690 and a specific gravity at 60° F. of 0.8911.

Compression Molding

Samples were melted at 190° C. for 3 min. and compression molded at 190° C. under 20,000 lb (9,072 kg) of pressure for another 2 min. Subsequently, the molten materials were quenched in a press equilibrated at room temperature.

Differential Scanning Calorimetry (DSC)

A Dupont DSC-2210 was used to measure the thermal transition temperatures and heat of transition for the samples. In order to eliminate previous thermal history, samples were first heated to about 160° C. Heating and cooling curves were recorded at 10° C./min. Melting (T_m from second heat) and crystallization (T_c) temperatures were recorded from the peak temperatures of the endotherm and exotherm, respectively.

Dynamic Mechanical Spectroscopy (DMS)

Dynamic mechanical data were generated using a Rheometrics RSA-II solid state analyzer, and melt pressed (~20 mil (0.0508 cm) thick) film test specimens. The DMS measurements were conducted at a step rate of 5° C./min and a fixed frequency of 10 rad/sec. The glass transition temperature (T_g) of the samples was determined from the $\tan \delta$ peak maximum.

Shear Rheology

Oscillatory shear rheology measurements were performed with a Rheometrics RMS-800 rheometer. Melt rheological properties were monitored at an isothermal set temperature of 190° C. in a frequency sweep mode, using parallel plate test geometry.

Mechanical Testing

Tensile properties of the compression molded samples were measured using an Instron 1145 tensile machine equipped with an extensometer. ASTM-D638 samples were tested at a strain rate of 5 min⁻¹. Micro-tensile samples were tested at a speed of 5 in/min (12.7 cm/min) at -10° C. Average of four tensile measurements is given. The standard deviation for the ultimate properties is typically about 10% of the reported average value.

Tensile Stress Relaxation

Uniaxial tensile stress relaxation was evaluated using an Instron 1145 tensile machine. Compression molded film (~20 mil (0.0508 cm) thick) with a 1" (2.54 cm) gauge length was deformed to a strain level of 50% at a strain rate of 20 min⁻¹. The force required to

maintain 50% elongation was monitored for 10 min. The magnitude of the stress relaxation is defined as $((f_i - f_f)/f_i)$ where f_i is the initial force and f_f is the final force.

EXAMPLES 1 TO 6 AND COMPARATIVE EXPERIMENT A

Six blend compositions, examples 1, 2, 3, 4, 5 and 6, are prepared from interpolymer (A) above and either a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester (P610, available from the C.P.Hall Company, and having a molecular weight (MW) about 400) or mineral oil (Sunpar 2280, a paraffinic oil available from Sun Company, Inc. and having a molecular weight of 690 and a specific gravity at 60° F. of 0.8911) or polymeric glutarate (G57 available from the C.P.Hall Company) in weight ratios given in Table 2 with a Haake mixer equipped with a Rheomix 3000 bowl. About 180 grams of the dry blended component materials were fed into the mixer equilibrated at 150° C. Feeding and temperature equilibration took about 3-5 minutes. The molten material was mixed at 150° C. and 40 rpm for 10 minutes.

The characterization data for the examples and the component interpolymer are given in Table 2. It was possible to modify the interpolymers, and produce materials with structural integrity and good mechanical properties.

Analysis of examples 4 and 5 of modification with the P610 phthalate ester shows the good plasticization achieved. There is no significant broadening of the Tan .delta. of the loss peak associated with the interpolymer glass transition process. These modified interpolymers show good low temperature performance, and significant retention of stress relaxation behavior. The level of hardness can be controlled by appropriate selection of plasticizer. The combination of mechanical properties, relaxation behavior, hardness and processability is particularly desirable, for example in many film applications.

TABLE 2

Example or Comparative Experiment										
A*	1	2	3	4	5	6				
Wt ratio	100/0	95/5	90/10							
80/20										
Interpolymer										
(A)**/Mineral oil										
Wt ratio	90/10									
80/20										
Interpolymer (A)/										
P610 plasticizer										
Wt ratio	90/10									
Interpolymer (A)/										
G57 glutarate										
Tg (DMS), °C.	30	22	22	21	7	4.5	24			
Tan .delta. peak width	16	15								
at half height										
deg. C.										
Mechanical Prop-										
erties (@ 23° C.)										
Tensile Mod,	617.6	6.4	6.8	6.3	2.4	0.94	7.4			
MPa										
% Strain @	257	313	290	310	370	546	273			
Break										
Total energy @	122.4	21.6								
Break, N.m										
Mechanical Prop-										
erties										
(@ -10° C.)										

Tensile Mod,
MPa
% Strain @
18.6 281
Break
Total energy @
9.9 145.6
Break, N.m
% Stress 92.9 68.7
Relaxation
(@ 23° C.)
Hardness: 96 95 92 92 66 49 96
Shore A
(@ 23° C.)
Melt Rheology
(190° C.)
10⁵ .eta. (0.1 rad/
6.53 0.17
sec), Poise
.eta. (100/0.1)
0.048 0.11
Tan .delta. (0.1
4.42 10.2
rad/sec)

*Not an example of the present invention.

**Interpolymer (A) is an ethylene/styrene interpolymer containing 69.4 weight percent (37.9 mole percent) styrene (measured by NMR technique), having an I₂ melt flow index of 0.18 and containing 8.4 weight percent atactic polystyrene. The polymer showed no measurable crystallinity by DSC techniques.

As a further comparative experiment, a blend of polystyrene (PS; Styron.TM. 685D, a polystyrene having a Melt Flow Index (200° C./5.0 kg) of 1.5 g/10 min and a specific gravity of 1.04, commercially available from The Dow Chemical Company) and P610 plasticizer was produced in a PS/P610 weight ratio of 80/20. This produced a material which had a Tg of 37° C. compared to 106° C. for the unmodified PS. No properties could be measured due to the form of this composition, confirming past experience that phthalate esters do not function as effective plasticizers in PS.

EXAMPLES 7 & 8 and COMPARATIVE EXPERIMENT B

Two blend compositions, examples 7 and 8, are prepared from interpolymer (B) above and a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester (P610, available from the C.P.Hall Company, and having a molecular weight (MW) about 400) in weight ratios given in Table 3 with a Haake mixer equipped with a Rheomix 3000 bowl. About 180 grams of the dry blended component materials were fed into the mixer equilibrated at 150° C. Feeding and temperature equilibration took about 3-5 minutes. The molten material was mixed at 150° C. and 40 rpm for 10 minutes.

The characterization data for the examples and the component Interpolymer are given in Table 3. It was possible to modify the interpolymers, and produce materials with structural integrity and good mechanical properties.

Analysis of examples 7 and 8 of modification with the P610 phthalate ester shows the good plasticization achieved. There is no significant broadening of the Tan .delta. of the loss peak associated with the interpolymer glass transition process. These modified interpolymers show good low temperature performance, and surprising retention of stress relaxation behavior. The combination of mechanical properties, relaxation behavior, hardness and processability is particularly desirable, for example in many film applications.

TABLE 3

Example or Comparative Experiment B* 7 8
Wt ratio 80/20 70/30
Interpolymer (B)**/P610 plasticizer
Tg (DMS), °C. 29.8 7.5 -10.8
Tan.delta. peak width at half height 15 18 17 deg. C.
Mechanical Properties (@ 23° C.)
Tensile Mod, Mpa 617.6 1.7 0.6
% Strain @ Break 248 587 320
Total energy @ Break, N.m 101.4 8.7 1.4
Mechanical Properties (@ -10° C.)
Tensile Mod, Mpa
% Strain @ Break 5.7 249 403
Total energy @ Break, N.m 9.9 100 32.1
% Stress Relaxation (@ 23° C.) 93.5 78.5 90.7
Hardness: Shore A (@ 23° C.) 98 37 21
Melt Rheology (190° C.)
10 ⁵ .eta. (0.1 rad/sec), Poise 1.01 0.19 0.082
.eta. (100/0.1) 0.14 0.29 0.36
Tan .delta. (0.1 rad/sec) 9.98 21.0 25.3

*Not an example of the present invention.

**Interpolymer (B) is an ethylene/styrene interpolymer containing 69.9 weight percent (38.4 mole percent) styrene (measured by NMR technique), having an I₂ melt flow index of 1.83 and containing 8.2 weight percent atactic polystyrene. The polymer shows no measurable crystallinity by DSC techniques.

EXAMPLE 9 and COMPARATIVE EXPERIMENT C

Example 9 is prepared from interpolymer (C) above and a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester (P610, available from the C.P.Hall Company, and having a molecular weight (MW) about 400) in weight ratios given in Table 4 with a Haake mixer equipped with a Rheomix 3000 bowl. About 180 gram of the dry blended component materials were fed into the mixer equilibrated at 150° C. Feeding and temperature equilibration takes about 3-5 minutes. The molten material is mixed at 150° C. and 40 rpm for 10 minutes.

The characterization data for the example and the component Interpolymer are given in Table 4. The modified interpolymers has structural integrity and good mechanical properties. The solid materials shows increased crystallinity compared to the unmodified interpolymer. There is some broadening of the Tan .delta. of the loss peak associated with the interpolymer glass transition process, which could find utility in some energy absorbing applications. The modified interpolymers show good low temperature performance, and retention of stress relaxation behavior. The combination of mechanical properties, relaxation behavior, hardness and processability is again desirable, for example in many film applications.

TABLE 4

Example or Comparative Experiment C* 9
Wt ratio 80/20
Interpolymer (C) **/P610

plasticizer
 DSC data
 Percent crystallinity
 4.7 10.5
 Tm °C. 45.7 44.8
 Tg (DMS), °C. -2.2 -21.7
 Tan .delta. peak width at half height
 15 22
 deg. C.
 Mechanical Properties (@ 23° C.)
 Tensile Mod, Mpa 6.8 4.1
 % Strain @ Break 475 557
 Total energy @ Break, N.m
 105.6 65.2
 Mechanical Properties (@ -10° C.)
 Tensile Mod, Mpa 81.9 8.8
 % Strain @ Break 258 480
 Total energy @ Break, N.m
 79.2 160.7
 % Stress Relaxation (@ 23° C.)
 26.2 29.6
 Hardness: Shore A (@ 23° C.)
 75 52
 Melt Rheology (190° C.)
 10⁵ .eta. (0.1 rad/sec), Poise
 31 0.094
 .eta. (100/0.1) -- --
 Tan .delta. (0.1 rad/sec)
 4.2 2.1

*Not an example of the present invention.

*Interpolymer (C) is an ethylene/styrene interpolymer containing 47.3 weight percent (19.5 mole percent) styrene, having an I₂ melt flow index of 0.01 and containing 3.7 weight percent atactic polystyrene.

EXAMPLES 10 & 11 AND COMPARATIVE EXPERIMENT D

Two blend compositions, examples 10 and 11, are prepared from interpolymer (D) above and either a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester (P610, available from the C.P. Hall Company, and having a molecular weight (MW) about 400) or mineral oil (Sunpar 2280, a paraffinic oil available from Sun Company, Inc. and having a molecular weight of 690 and a specific gravity at 60° F. of 0.8911) in weight ratios given in Table 5 with a Haake mixer equipped with a Rheomix 3000 bowl. About 180 gram of the dry blended component materials were fed into the mixer equilibrated at 150° C. Feeding and temperature equilibration takes about 3-5 minutes. The molten material is mixed at 150° C. and 40 rpm for 10 minutes.

The characterization data for the examples and the component Interpolymer are given in Table 5. The modified interpolymers have structural integrity and good mechanical properties.

The oil is a more effective modifier for lowering Tg in this Interpolymer compared to Interpolymer (A).

The solid materials show small changes in level of crystallinity compared to the unmodified interpolymer. Both modifiers produce broadening of the Tan .delta. of the loss peak associated with the interpolymer glass transition process, which could find utility in some energy absorbing applications.

The modified interpolymers show good low temperature performance, and retention of stress relaxation behavior. The processability is much altered, particularly the viscosity, and this translates into improved processability in some applications.

TABLE 5

Example or Comparative Experiment
D* 10 11

Wt ratio Interpolymer 80/20

(D**)/Mineral oil
Wt ratio Interpolymer (D)/P610 80/20
plasticizer
Percent crystallinity (DSC data)
14.7 20.7 17.8
Tm °C. (DSC data)
71.3 69.7 70.4
Tg (DMS), °C.
-8 -14.5 -25.4
Tan.delta. peak width at half height
23 34 39
deg. C.
Mechanical Properties (@ 23° C.)
Tensile Mod, MPa 19.7 2.1 12.6
% Strain @ Break 378 396 493
Total energy @ Break, N.m
150 82.7 65.2
Mechanical Properties (@ -10° C.)
Tensile Mod, MPa 66.6 2.0 27.2
% Strain @ Break 303 403 484
Total energy @ Break, N.m
91.0 32.1 148
% Stress Relaxation (@ 23° C.)
26.2 26.1 26.3
Hardness: Shore A (@ 23° C.)
96 92 49
Melt Rheology (190° C.)
10⁵ .eta. (0.1 rad/sec), Poise
16.6 0.43 0.43
.eta. (100/0.1) 0.16 0.19 0.20
Tan .delta. (0.1 rad/sec)
2.37 2.7 2.6

*Not an example of the present invention.

**Interpolymer (D) is an ethylene/styrene interpolymer containing 29.3 weight percent (10 mole percent) styrene, having an I₂ melt flow index of 0.03 and containing 1 weight percent atactic polystyrene.

Foreign References: **none**

(No patents reference this one)

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